Available online at www.sciencedirect.com
ScienceDirect
Environmental Pollution 150 (2007) 306–312
ENVIRONMENTAL POLLUTION
www.elsevier.com/locate/envpol

Acceleration of selenium volatilization in seleniferous agricultural drainage sediments amended with methionine and casein

G.S. Bañuelos [a,*], Z.-Q. Lin [b]

[a] USDA-ARS, Water Management Research Laboratory, Parlier, CA 93648, USA
[b] Department of Biological Sciences & Environmental Sciences Program, Southern Illinois University Edwardsville, Edwardsville, IL 62026-1651, USA

Received 28 November 2006; received in revised form 29 January 2007; accepted 4 February 2007

Amending drainage sediment with either methionine or casein promotes the volatilization of selenium.

Abstract

Phytoremediation is potentially effective for managing excessive selenium (Se) in drainage sediment residing in the San Luis Drain in central California. This 2-year field study examined the feasibility of amending drainage sediment (containing 4.78 $\mu g\ Se\ g^{-1}$) with methionine and casein to enhance volatilization without or with vegetation of *Sporobolus airoides*. Results show that without organic amendments, rates of Se volatilization were less than 25 $\mu g\ m^{-2}\ d^{-1}$ in all plots. After amending the sediment with 71.4 mg methionine kg^{-1} soil, Se volatilization rates were $434 \pm 107\ \mu g\ m^{-2}\ d^{-1}$ in vegetated plots and $289 \pm 117\ \mu g\ m^{-2}\ d^{-1}$ in irrigated bare plots. With the amendment of 572 mg casein kg^{-1} soil, rates increased to $346 \pm 103\ \mu g\ m^{-2}\ d^{-1}$ in irrigated bare plots and to $114 \pm 55\ \mu g\ m^{-2}\ d^{-1}$ in vegetated plots. Both methionine and casein promoted biological remediation of Se via volatilization most effectively during the warmest months.

Keywords: Drainage sediments; Selenium; Volatilization; Methionine and Casein

1. Introduction

Selenium (Se) contamination of agricultural drainage is an important environmental issue in the western United States. Metalloid Se, a naturally occurring trace element, is primarily found in sedimentary and shale rock formations in the San Joaquin Valley (SJV) of central California. The accumulation of bioavailable Se to high concentrations in aquatic systems results in damage to wildlife, as illustrated by the environmental Se disaster at the Kesterson National Wildlife Refuge in the San Joaquin Valley (Ohlendorf et al., 1986). Therefore, the management and remediation of large quantities of Se-contaminated drainage sediments in the San Luis Drain (SLD) is a major public concern (Bañuelos et al., 2005; Zawislanski et al., 2003). At present, there is no satisfactory technology available to remediate the Se toxicant in the sediments.

The San Luis Drain was built in the late 1970s for the transport of Se-laden agricultural drainage from the western San Joaquin Valley to the Kesterson Reservoir, containing small sloughs, and out toward the San Francisco Bay Delta via the San Joaquin River. The SLD was abandoned due to strong public objections and the new State agricultural drainage discharge regulation because of Se toxicity to wildlife observed at the Kesterson Reservoir in the early 1980s. This left large quantities of Se-, salt-, and boron-contaminated sediment in the SLD. Clearly, the toxic sediments need to be properly managed and remediated. Removing and landfill-disposing of the sediment is prohibitively expensive – ranging from 1.1 to 3.4 million dollars per 100,000 m^3 (Zawislanski et al., 2003). Other methods, such as soil/sediment washing and the reburial of the contaminated sediment are also cost-intensive.

Land disposal of drainage sediment may be an option to consider due to its low cost and the proximity of available land in the SJV. In this regard, a pilot-scale test for the land disposal of Se-enriched sediments from the SLD was evaluated in

* Corresponding author.
E-mail address: gbanuelos@fresno.ars.usda.gov (G.S. Bañuelos).

0269-7491/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.envpol.2007.02.009

the San Joaquin Valley (Zawislanski et al., 2003). They concluded that the overall low Se solubility within the sediment limited the movement of Se below 0–15 cm. To complement this mode of disposing of Se-contaminated sediments, Bañuelos and Lin (2005) suggested that phytoremediation of Se may also be an effective strategy to eventually lower the Se content. The potential management of the residual Se in the drainage sediment with plants would involve both phytoextraction and biological volatilization of Se, therefore, this requires identifying plant species that can tolerate high levels of salinity and soluble B.

The volatilization of Se by plants and soil microbes is an important component of phytoremediation, where Se dissipates from Se-laden drainage sediments to the atmosphere (Bañuelos et al., 2005; Frankenberger et al., 2004; Lin and Terry, 2003; Lin et al., 2000). Volatile Se compounds (mainly dimethyl selenide and dimethyl diselenide) form through biomethylation, a biological process in which microorganisms and/or plants convert inorganic Se into methylated volatile Se compounds (Terry et al., 1992, 2000; Zieve and Peterson, 1984; Lewis et al., 1974). The final methylated selenide compounds are subject to volatilization losses into the atmosphere. Volatilization of Se from contaminated sites is favorable from an environmentally sustainable perspective. This is because it simultaneously lowers the amount of Se available for entry into food chains (Zayed et al., 2000; Losi and Frankenberger, 1997) and dimethyl selenide (DMSe) is some 500 times less toxic to rats than the inorganic forms of Se (Wilber, 1980; McConnell and Portman, 1952). Moreover, Se is an essential element to humans that is deficient in many soils. Aerial translocation of Se may even be beneficial to downwind communities where soils are deficient in Se (Lin et al., 2000).

Earlier studies showed that biological volatilization of Se varies greatly because of fluctuations in different physical, chemical, and biological factors in the field (Lin and Terry, 2003; Zhang and Frankenberger, 1999; Hansen et al., 1998; Rael et al., 1996; Frankenberger and Karlson, 1989, 1994a,b; Jayaweera and Biggar, 1992). For instance, higher rates of Se volatilization often occurred when temperature, soil water content, and available organic carbon in soil were high (Bañuelos et al., 2005; Lin and Terry, 2003; Lin et al., 2000; Frankenberger and Karlson, 1994b). To enhance the levels of Se volatilization, Frankenberger and Karlson (1989) have amended seleniferous soils with different types of organic C sources to increase soil microbial activities associated with Se volatilization. With soil amendments, such as orange peels and a protein mixture, the decomposition of organic matter produces methyl donors, which enhance Se methylation process and, therefore, increase the production of the volatile Se compounds of DMSe and dimethyl diselenide (DMDSe). According to the suggested metabolism and volatilization pathway of Se (Terry et al., 2000), both methionine and casein may provide methyl groups for the methylation process that eventually results in the formation of volatile DMSe (Zhang and Frankenberger, 1999). Similarly, studies by Thompson-Eagle and Frankenberger (1990), Frankenberger et al. (2004), and Calderone et al. (1990) showed that, under greenhouse conditions, and in water, the addition of casein (0.1%), pectin, and other organic amendments have effectively promoted Se volatilization (up to 800 $\mu g\ m^{-2}\ d^{-1}$) in unvegetated sediments from Kesterson Reservoir (Zhang and Frankenberger, 1999). However, the extent to which Se can be removed from agricultural drainage sediment in the SLD via biological volatilization, especially in light of high levels of Se, B, S, and salts, has only been explored preliminarily under field conditions. Bañuelos et al. (2005) observed relatively low rates of volatilization ranging from 14 to 39 $\mu g\ Se\ m^{-2}\ day^{-1}$ from different plant species planted in the drainage sediment. In order to implement the technology of biological volatilization for removing substantial amounts of Se from drainage sediment, it is imperative to explore ways to accelerate the rate of Se volatilization. Hence, the purpose of this field study was to determine the effects of adding different concentrations of methionine and casein on Se volatilization produced from the bare or vegetated drainage sediment plots over time.

2. Methods and materials

2.1. Field test plots

The drainage sediment was collected from the top 250 mm layer of sediment in the San Luis Drain, near Mendota of central California. The collected drainage sediment was spread to a depth of 400 mm in a previously excavated field plot at the USDA Research Facility in Parlier, CA in 1999 (Bañuelos et al., 2005). The drainage sediment was covered with a 40 mm layer of clean sandy loam soil (pH of 7.2, EC of 0.9 $dS\ m^{-1}$, and total Se concentrations of $<0.1\ mg\ kg^{-1}$) to enhance biological activity and encourage plant growth and survival. In April 2004 and 2005, soil samples were collected in triplicate to a depth of 0–250 mm, the zone of primary Se volatilization. The major soil chemical properties were as follows ($n = 18$): total Se ($\mu g\ g^{-1}$) of 4.78 ± 1.0, extractable Se ($\mu g\ mL^{-1}$) of 0.25 ± 0.01, extractable B ($\mu g\ mL^{-1}$) of 5.61 ± 0.98, EC ($mS\ cm^{-1}$) of 4.82 ± 0.95, and pH of 8.21 ± 0.14.

2.2. Field site

Cultural beds were created with dimensions of 33-m long and 1-m wide (Bañuelos et al., 2005). The vegetated plots consisted of 2–3-year old established salado grass (*Sporobolus airoides*), which was selected for its high salt tolerance, hardiness, and low maintenance characteristics. The plants were dormant from December through March. Normal agronomic management practices were applied on the test plots throughout each growing season, such as annual application of 50 $kg\ ha^{-1}$ of non-sulfur containing ammonium nitrate fertilizer (NPK of 15-15-15), insect and animal (gopher) control, manual removal of weeds, and interval clipping (generally four times during the growing seasons).

A surface-drip irrigation system was installed consisting of one in-line turbulent flow emitter per bed with an emitter spacing of 0.45 m and a discharge rate of 4 $L\ h^{-1}$. All irrigated plots were drip-irrigated based on both evaporation and evapotranspiration losses recorded for bare plots and for vegetated plots located in duplicate on adjacent 15 × 1 m non-drainage sediment plots (sandy loam soil), and also from the weather data collected from California Irrigation Management Information System (CIMIS) weather station located about 2-km away from the field site. Fig. 1 shows the local meteorological conditions during the course of 210-day field study in 2005, including averaged air and soil temperatures and total precipitation.

2.3. Organic amendments

To determine the effective levels of different soil amendments for potentially promoting the greatest amount of volatile Se during the summer months of 2004, solutions of L-methionine (tissue culture grade, 98% purity, Fisher

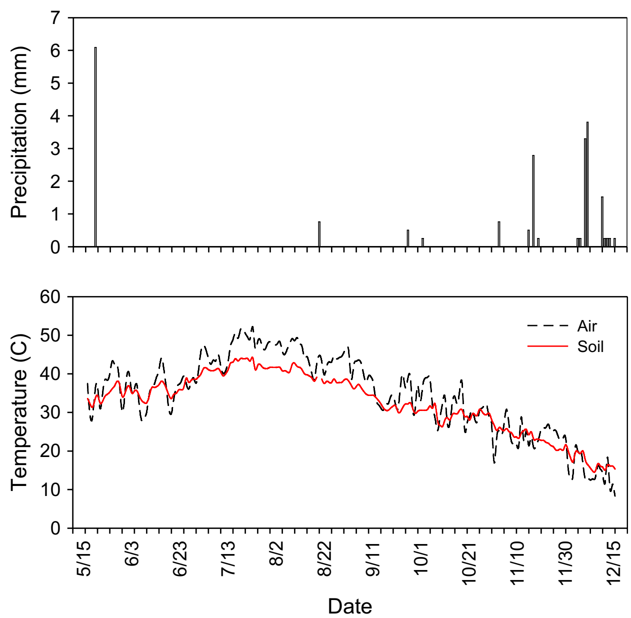

Fig. 1. Air, soil temperature (bottom), and total precipitation (top) at the field study site during the course of the 210-day field experiment in 2005. Data were obtained from a CIMIS located 2 km from this field study.

Scientific, Fairlawn, NJ) were prepared at concentrations of 1.4, 14.3, and 71.4 mg kg^{-1} dry soil. Each of the concentrations was respectively applied to vegetated, irrigated bare, and non-irrigated bare plots (described later). The rates of Se volatilization were measured at Day 1 (24 h) and Day 7 (168 h), respectively, after the addition of methionine. Two liter solutions of casein were prepared from vitamin D homogenized/pasteurized low fat milk containing 26 g casein L^{-1} (www.foodsci.com) and prepared to give the following concentrations: 29, 143, 286, and 572 mg kg^{-1} dry soil. Each of the concentrations was respectively applied to both vegetated and irrigated bare plots in 7-day intervals for 35 days in 2004, and the rates of Se volatilization were measured for 24 h, respectively.

To determine the Se volatilization in the long term, the highest concentration of both methionine and casein was then applied, respectively, in 7–10-day intervals to both vegetated and irrigated bare plots, and rates of Se volatilization were periodically measured for 210 days during May 15–November 15, 2005. The control plots received 2 L deionized water without either methionine or casein as an organic amendment. Both organic amendments in solution were applied onto a 0.5 m^2 area to a depth of 0–150 mm, as measured by the wetted zone within the volatilization chamber (description below). The total mass of the treated sediment/soil (0.5 m^2 surface area × 150 mm depth) was 70 kg dry weight. This measured value was used for the calculation of treatment concentrations that were described above for both methionine and casein.

Prior to volatile Se measurement, soil moisture levels in the top 150-mm layer were determined and maintained at 18–20% (w/w). The selected methionine or casein concentrations were, respectively, applied onto the sediment within a 0.5 m^2 area prior to placing the sampling chamber at the sites. Using volatile sulfur, which is chemically similar to Se, as an indicator of the effects induced by the addition of either methionine or casein, we pre-determined that the amendment effects on volatile Se disappeared after 6 days, irrespective of the amendment concentrations (data not shown). Hence, we repeated the experiment with the same application sites after a waiting period of at least 7 days. The treatments and control sampling sites with no organic amendments were rotatiled to a depth of 150 mm.

2.4. Measurement of Se volatilization

The measurement of Se volatilization in this field study was conducted with an open-through chamber system that has been applied in several other field studies (Bañuelos et al., 2005; Lin and Terry, 2003; Lin et al., 2002). Briefly, the chambers used for volatile Se collection were made of 6.6-mm thick Plexiglas and had dimensions of 0.71 m long, 0.71 m wide and 0.76 m high, as described in detail by Lin et al. (1999). Each chamber enclosed an area of 0.5 m^2 and had an internal volume of 0.38 m^3. Volatile Se was trapped in an alkaline peroxide trap solution (6% H_2O_2 and ~0.05 M NaOH). The solutions were contained in a series of three 500-ml gas-washing bottles containing 200 ml of the trap solution. The gas-washing bottles were connected to the outlet port of each chamber and to each other with Teflon tubing. The volatile Se produced inside each chamber was captured by pulling air out of the chamber through the trap solution with a 1/3-hp vacuum pump. Solutions from three gas-washing bottles were collected and taken to the lab for Se analysis (Lin et al., 2002). The recovery rate of this sampling method under the field conditions ranged from 94 to 96% and there was no breakthrough of volatile Se from the trapping system.

The trap solutions were replaced every 24 h in this study. The Se concentrations in trap solutions were determined by an atomic absorption spectrophotometer (Thermo Jarrell Ash, Smith Hieftje 1000, Franklin, MA) with an automatic vapor accessory (AVA 880). The volatilization rate was calculated with a flux unit (μg Se m^{-2} d^{-1}) over a ground surface area in the fields with different soil amendment treatments.

2.5. Statistical analysis

Statistical Analysis System (SAS, version 6.03) was used for the data analysis (SAS Inst., 1988), and Duncan's multiple range test was applied to treatment means at $\alpha = 0.05$, the level of significance (Gomez and Gomez, 1984).

3. Results

3.1. Effects of methionine amendments

Selenium volatilization significantly increased with the addition of methionine to both irrigated bare and vegetated plots in the summer of 2004 (Table 1). The greatest rates of Se volatilization were measured with the addition of 71.4 mg methionine kg^{-1} dry soil, especially in the vegetated plot. Rates of Se volatilization decreased significantly from Day 1 to Day 7 at both vegetated and irrigated bare plots ($P < 0.05$). For example, the rate of Se volatilization during Day 1 was 434 ± 107 μg m^{-2} d^{-1} in the irrigated vegetated

Table 1
Rates (μg Se m^{-2} d^{-1}) of Se volatilization in non-irrigated bare drainage sediment, irrigated bare drainage sediment, and irrigated drainage sediment with vegetation at 24 h and 168 h after amending the sediment with methionine

Methionine (mg/kg dry soil)	Volatile Se (μg Se m^{-2} d^{-1})					
	Bare sediment, no irrigation		Bare sediment, irrigated		Salado grass, irrigated	
24 h post application						
0	10	(1) a	24	(14) c	44	(9) d
1.4	9	(1) a	79	(46) b	179	(105) c
14.3	8	(2) a	246	(67) a	378	(98) b
71.4	12	(2) a	289	(117) a	434	(107) a
168 h post application						
0	10	(1) a	28	(14) b	20	(6) c
1.4	12	(2) a	26	(13) b	31	(11) b
14.3	9	(2) a	17	(8) c	33	(8) b
71.4	11	(1) a	58	(30) a	104	(62) a

Values are the mean from six replications with the standard deviation in parenthesis. Means followed by the same letter are not significantly different ($P > 0.05$).

plots and $289 \pm 117\ \mu g\ m^{-2}\ d^{-1}$ in the irrigated bare plots. During Day 7, the rates of Se volatilization were $104 \pm 62\ \mu g\ m^{-2}\ d^{-1}$ and $58 \pm 30\ \mu g\ m^{-2}\ d^{-1}$ in the vegetated and irrigated bare plots, respectively (Table 1).

The results for the 210-day growing season in 2005 showed that the addition of methionine ($71.4\ mg\ kg^{-1}$) on a continued basis to sediment/soil significantly promoted Se volatilization in both vegetated and irrigated bare sediment plots (Fig. 2 and Table 2). For example, the average rate of Se volatilization in the vegetated sediment was $162 \pm 106\ \mu g\ m^{-2}\ d^{-1}$ and $94 \pm 49\ \mu g\ m^{-2}\ d^{-1}$ in the irrigated bare sediment. However, without the organic amendments, the average rate of Se volatilization generally did not exceed $50\ \mu g\ m^{-2}\ d^{-1}$ in the vegetated plots, and also did not exceed $25\ \mu g\ m^{-2}\ d^{-1}$ or $12\ \mu g\ m^{-2}\ d^{-1}$ in the irrigated and non-irrigated bare sediment plots, respectively (Fig. 2). The greatest rates of volatilization occurred during the summer months or the warmest season of the year (July 18–August 17) in both irrigated bare and vegetated sediment plots (Fig. 2).

3.2. Effects of casein amendments

Increasing concentrations of casein applied onto vegetated and irrigated bare sediment plots resulted in significantly greater rates of Se volatilization, especially in bare irrigated plots of summer 2004 (Table 3). The highest casein application rate resulted in the greatest rates of Se volatilization, which was consistently 2–3 times greater in the bare irrigated plots than the vegetated plots (Table 3). With the addition of different concentrations of casein in the soil/sediment, rates of Se volatilization were consistent during a 35-day testing period in 2004 with a reapplication at 7-day intervals (Table 3).

The addition of 572 mg casein kg^{-1} dry soil for the 210-day growing season in 2005 significantly increased Se volatilization, especially in irrigated bare plot (Fig. 3 and Table 2). The seasonal production of volatile Se in 2005 was similar to the trend observed with the methionine treatments; the greatest rates of Se volatilization occurred during the warm summer months in both irrigated bare and vegetated sediment fields (Fig. 3).

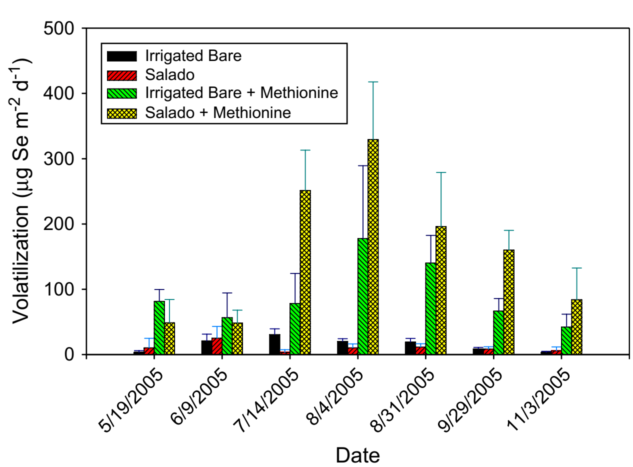

Fig. 2. Rates of Se volatilization in vegetated and bare irrigated drainage sediment amended periodically with methionine ($71.4\ mg\ kg^{-1}$ dry soil) during a 210-day field experiment in 2005. The figure includes the average and standard deviation of each variable observed.

Table 2
Differences in Se volatilization among the treatments, including the irrigated bare or vegetated drainage sediment amended with methionine ($71.4\ mg\ kg^{-1}$ dry soil) or casein ($572\ mg\ kg^{-1}$ dry soil) during a 210-day study in 2005

Treatments	BI	BIC	BIM	SG	SGC
BIC	0.02				
BIM	0.004				
SG	ns	0.04	0.005		
SGC	0.02	ns	ns	0.03	
SGM	0.009	0.009	0.05	0.01	0.03

Values are the probability of hypothesis-testing error (or P values). BI: bare irrigated sediment, BIC: bare irrigated sediment amended with casein, BIM: bare irrigated sediment amended with methionine, SG: salado grass vegetated sediment, SGC: salado grass vegetated sediment amended with casein, SGM: salado grass vegetated sediment amended with methionine, and ns: no significant difference between the treatments ($P > 0.05$).

4. Discussion

The experimental drainage sediment in this study has been stabilized in the field for approximately 5 years, while subjected to various natural processes, including weathering, precipitation, leaching, decomposition of organic matter, and Se volatilization since 1999. Without any manipulation or amendment treatments to the sediment/soil under naturally occurring environmental conditions, Bañuelos et al. (2005) observed that the rates of Se volatilization were less than $50\ \mu g\ Se\ m^{-2}\ d^{-1}$ in drainage sediment plots supporting different plant species without the addition of any organic amendments, e.g., methionine or casein. In the present study, our results clearly show that both the addition of methionine and casein to the soil enhanced Se volatilization at least sixfold in either vegetated or

Table 3
Rates ($\mu g\ Se\ m^{-2}\ d^{-1}$) of Se volatilization in the drainage sediment amended with casein

Casein ($mg\ kg^{-1}$ dry soil)	Repeated measures after each amendment in 7-day intervals					Overall average
	1	2	3	4	5	
Irrigated bare sediment						
0	13	17	12	7	12	12 (3) e
29	27	30	33	30	25	29 (3) d
143	65	81	79	97	120	88 (21) c
286	217	125	146	375	216	216 (98) b
572	238	332	511	360	288	346 (103) a
Sediment vegetated with salado grass						
0	13	6	10	19	9	11 (5) c
29	11	6	14	19	10	12 (5) c
143	17	20	28	28	13	21 (7) b
286	39	37	10	22	27	27 (12) b
572	58	94	205	119	95	114 (55) a

The amended drainage sediment plots, with vegetation (salado grass) versus without vegetation, were irrigated during the experimental period. Casein was applied to the sediment repeatedly every 7 days and volatilization measurements were conducted immediately after the amendment for 24 h.

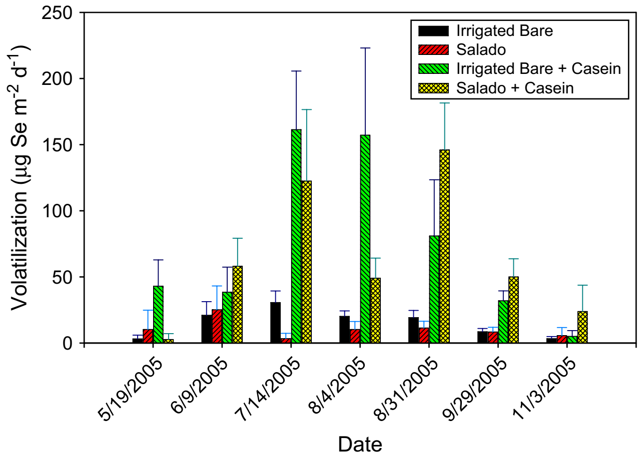

Fig. 3. Rates of Se volatilization in vegetated and bare irrigated drainage sediment amended periodically with casein (572 $mg\ kg^{-1}$ dry soil) during 210-day field experiment in 2005. The figure includes the average and standard deviation of each variable observed.

bare irrigated drainage sediment plots. In the summer of 2004 a high volatilization rate of 434 $\mu g\ Se\ m^{-2}\ d^{-1}$ was observed with the high application rate of methionine to drainage sediment plots grown to salado grass, while a consistent volatilization rate of 346 $\mu g\ Se\ m^{-2}\ d^{-1}$ was observed with the high application rate of casein to bare irrigated plots. Clearly, the natural process of biological volatilization of Se with or without plants can be accelerated with the addition of either methionine or casein to the irrigated drainage sediment. Importantly, one may expect that greater the concentrations of reduced forms of Se present in the sediment/soil the easier it may be for the volatilization of Se to occur (Terry et al., 2000). In this regard, neither methionine nor casein's potential in reducing Se to such forms as selenite or selenide in the sediment was not considered in this study, nor were the concentrations of reduced forms of Se identified.

One may speculate that higher rates of volatile Se were produced from the vegetated plots with added methionine compared to bare irrigated plots because of additional microbial activity associated with salado grass. In this regard, it is well known that plants produce root exudates containing organic acid anions, sugars, vitamins, amino acids, inorganic ions, and some enzymes, which likely have substantial impacts on microbial population development and bioactivity in the rhizosphere. Since microbiological measurements were not performed in this study, we can only speculate that volatilizing microflora associated with salado grass, i.e., fungi and bacteria species (see Doran, 1982; Thompson-Eagle and Frankenberger, 1992) were able to volatilize Se to a greater degree when methionine was supplied. Due to physical constraints imposed by the volatilization chambers, we were unable to distinguish between microbial and plant volatilization of Se.

With either organic amendment, the addition of available carbon from both methionine and casein sources contributed to the accelerated evolution of volatile Se in both vegetated and unvegetated drainage sediment plots. Similarly, previous research performed by Frankenberger and Karlson (1995) on unplanted media has shown that the different organic amendments can stimulate microbial volatilization of Se. It was, however, beyond the scope of this paper to identify specific microorganisms and their volatilization activity associated with or without salado grass as affected by either organic amendment in a vegetated, or in bare irrigated drainage sediment plot. The role of microorganisms and plants on the biomethylation of Se has been previously reviewed by Chasteen and Bentley (2003).

In addition to organic amendments, the positive effect of soil water (i.e., irrigation) on the rate of Se volatilization was observed between bare irrigated and bare not irrigated drainage sediment plots amended with either methionine or casein. Generally, without irrigation there was no effect of either organic amendment on the rate of Se volatilization. Others have observed that soil microbial activity was much higher after wetting a dry soil (Orchard and Cook, 1983), and consequently Se volatilization was greater (Zieve and Peterson, 1981; Zhang and Frankenberger, 1999; Zhang et al., 1999). In the present field study, the soil water content was maintained at 18–20% (w/w) 24 h prior to measurement, indicating that greater rates of Se volatilization may be achieved by incorporating drying–wetting irrigation cycles in the field (Shrestha et al., 2006; Zhang and Frankenberger, 1999).

Using available and inexpensive sources of organic amendments containing methionine and casein are desirable for promoting volatilization of Se on a large scale practice. For this reason, milk was used in this study as our source of casein. As an inexpensive and available source of methionine we tried adding frozen peas (containing 820 mg methionine kg^{-1} fresh weight) onto the bare irrigated drainage sediment plot. Our preliminary results did not show a substantial increase in Se volatilization (<20 $\mu g\ Se\ m^{-2}\ d^{-1}$; data not presented). The lack of response likely resulted from our improper field management practices associated with the addition of the peas as an amendment. With the future use of such organic materials as peas, more studies are needed to investigate the essential incubation and decomposition time, as well as effective ways to prevent insect and animal infestation of peas under field conditions.

The objective of this field trial was to facilitate the eventual reductions of Se levels in the contaminated soil/sediment disposed of onto soil via biological volatilization. Even though there are a number of uncertainties associated with the estimated phytoremediation efficiency, for illustrative purposes we estimated the time required to completely remove Se from the drainage sediment via biological volatilization measured under the described parameters. We assumed the following: 1 m^2 section of drainage sediment, 200 mm depth, a total dry weight of 208 $kg\ m^{-3}$, a mean Se concentration of 4.8 $mg\ Se\ L^{-1}$, and contained a total of 998 mg of Se. Assuming the highest volatilization rates of 434 and 289 $\mu g\ m^{-2}\ d^{-1}$ for a 210-day growing season in methionine-treated vegetated and bare plots, respectively, it would take 11 and 17 years to volatilize the total amount of Se from 0 to 200 mm in the vegetated and bare sediment plots, respectively (assuming the same rates of Se volatilization on an annual basis). Using the average Se volatilization rates of 114 and 346 $\mu g\ m^{-2}\ d^{-1}$

from the casein treated vegetated and bare sediment plots, respectively, it would take 42 and 14 years to dissipate the total Se from 0 to 200 mm depth from the vegetated and bare sediment plots to the atmosphere, respectively. Clearly, such approximations do not include potential losses of soluble Se occurring via plant accumulation, leaching, or decreases in Se volatilization due to forms of Se present in the soil, as well as the seasonal variation in Se volatilization. With this calculation and building upon the pioneering efforts exerted by other research groups (e.g., Frankenberger and Karlson, 1994a,b; Frankenberger, 2001; Terry and Zayed, 1998), we have clearly shown that biological volatilization of Se in any case is a natural process that can be manipulated with the addition of methionine and casein to a contaminated medium. More studies or attempts should be made with inexpensive and available organic amendments to elucidate potential long-term impacts on plant and soil microbial interactions to enhance Se volatilization under field conditions.

5. Conclusions

The biological Se volatilization in agricultural drainage sediment can be enhanced significantly by the soil amendments, such as methionine and casein, under field conditions, but with varying degrees of efficacy on irrigated vegetated and non-vegetated (i.e., bare sediment) plots. Rates of Se volatilization were greatest at the warmest times of the year for both organic amendments. Although rates of Se volatilization were lower in the vegetated plots with casein, milk as an organic amendment may be the most ideal because it is so readily available and is inexpensive.

Acknowledgements

This study was financially supported by California State University Agricultural Research Initiative (to Bañuelos) and Office of Science (BER), U.S. Department of Energy (to Lin, Grant No. DE-FG02-03ER63621). The authors are grateful to Mr. David Cone (Manager of Broadview Water District, Firebaugh, CA) for his support and assistance.

References

Bañuelos, G.J., Lin, Z.Q., 2005. Phytoremediation management of selenium-laden drainage sediments in the San Luis Drain: a greenhouse feasibility study. Ecotoxicology and Environmental Safety 62, 304–316.

Bañuelos, G.S., Lin, Z.Q., Arroyo, I., Terry, N., 2005. Selenium volatilization in vegetated agricultural drainage sediment from the San Luis Drain, Central California. Chemosphere 60, 1203–1213.

Chasteen, T.G., Bentley, R., 2003. Biomethylation of selenium and tellurium: microorganisms and plants. Chemical Reviews 103, 1–25.

Calderone, J.J., Frankenberger Jr., W.T., Parker, D.R., Karlson, U., 1990. Influence of temperature and organic amendments on the volatilization of selenium in sediments. Soil Biology and Biochemistry 22, 615–621.

Doran, J.W., 1982. Microorganisms and the biological cycling of selenium. Advanced Microbiology Ecology 6, 1–32.

Frankenberger Jr., W.T., Amrhein, C., Fan, T.W.M., Flaschi, D., Glator, J., Kartiner Jr., E., Kovac, K., Lee, E., Ohlendorf, H.M., Owens, L., Terry, N., Toto, A., 2004. Advanced treatment technologies in the remediation of seleniferous drainage waters and sediments. Irrigation and Drainage Systems 18, 19–41.

Frankenberger Jr., W.T., 2001. Dissipation of Soil Selenium by Microbial Volatilization at Kesterson Reservoir. U.S. Deptartment of the Interior, Bureau of Reclamation (Contract No. 7-FC-20–05240).

Frankenberger Jr., W.T., Karlson, U., 1989. Environmental factors affecting microbial production of dimethylselenide in a selenium-contaminated sediment. Soil Science Society of American Journal 53, 1435–1442.

Frankenberger Jr., W.T., Karlson, U., 1994a. Campaigning for bioremediation. Chemtech 24, 45–51.

Frankenberger Jr., W.T., Karlson, U., 1994b. Microbial volatilization of selenium from soil and sediments. In: Frankenberger Jr. W.T., Benson, S. (Eds.), Selenium in the Environment. Marcel Dekker, Inc, New York, pp. 369–387.

Frankenberger Jr., W.T., Karlson, U., 1995. Environmental factors affecting microbial production of dimethylselenide in a selenium-contaminated sediment. Soil Science Society of American Journal 53, 1435–1442.

Gomez, K.A., Gomez, A.A., 1984. Statistical Procedures for Agricultural Research, second ed. Wiley, New York.

Hansen, D., Duda, P.J., Zayed, A., Terry, N., 1998. Selenium removal by constructed wetlands: role of biological volatilization. Environmental Science and Technology 32, 591–597.

Jayaweera, G.R., Biggar, J.W., 1992. Extraction procedure for volatile selenium from activated carbon. Soil Science 153, 288–292.

Lewis, B.G., Johson, E.M., Broyer, T.C., 1974. Volatile selenium in higher plants. The production of dimethyl selenide in cabbage leaves by enzymatic cleavage of Se methyl selenomethionine selenonium salt. Plant and Soil 50, 107–118.

Lin, Z.-Q., Terry, N., 2003. Selenium removal by constructed wetlands: quantitative importance of biological volatilization in the treatment of Se-laden agricultural drainage water. Environmental Science and Technology 37, 606–615.

Lin, Z.-Q., Hansen, D., Zayed, A., Terry, N., 1999. Biological selenium volatilization: method of measurement under field conditions. Journal of Environmental Quality 28, 309–315.

Lin, Z.-Q., Schemenauer, R.S., Cervinka, V., Zayed, A., Lee, A., Terry, N., 2000. Selenium volatilization from the soil–plant system for the remediation of contaminated water and soil in the San Joaquin Valley. Journal of Environmental Quality 29, 1048–1056.

Lin, Z.-Q., Cervinka, V., Pickering, L.J., Zayed, A., Terry, N., 2002. Managing selenium-contaminated agricultural drainage water by the integrated on-farm drainage management system: role of selenium volatilization. Water Resolution 12, 3149–3159.

Losi, M.E., Frankenberger Jr., W.T., 1997. Bioremediation of selenium in soil and water. Soil Science 162, 692–702.

McConnell, K.P., Portman, O.W., 1952. Toxicity of dimethyl selenide in the rat and mouse. Proceedings of the Society for Experimental Biology and Medicine 79, 230–231.

Ohlendorf, H.M., Hoffman, D.J., Saiki, M.K., Aldrich, T.W., 1986. Embryonic mortality and abnormalities of aquatic birds: Apparent impact of selenium from irrigation drain water. Science Total Environment 52, 49–63.

Orchard, V.A., Cook, W.H., 1983. Relationship between soil respiration and soil moisture. Soil Biology and Biochemistry 15, 447–453.

Rael, R.M., Tuazon, E.C., Frankenberger Jr., W.T., 1996. Gas phase reaction of dimethyl selenide with ozone and the hydroxyl and nitrate radicals. Atmospheric Environment 30, 1221–1232.

SAS Institute. (1988) SAS procedures guide. Version 6.03 Edition. Statistical Analysis Systems Institute, Inc., Cary, NC, pp. 441.

Shrestha, B., Lipe, S., Johnson, K.A., Zhang, T.Q., Retzlaff, W., Lin, Z.-Q., 2006. Soil hydraulic manipulation and organic amendment for the enhancement of selenium volatilization in a soil–pickleweed system. Plant and Soil 288, 189–196.

Terry, N., Carlson, C., Raab, T.K., Zayed, A.M., 1992. Rates of selenium volatilization among crop species. Journal of Environmental Quality 21, 341–344.

Terry, N., Zayed, A., 1998. Phytoremediation of selenium. In: Frankenberger Jr. W.T., Engberg, R.A. (Eds.), Environmental Chemistry of Se. Marcel-Dekker, New York, pp. 633–656.

Terry, N., Zayed, A.M., De Souza, M.P., Tarun, A.S., 2000. Selenium in higher plants. Annual Review of Plant Physiology and Plant Molecular Biology 51, 401−432.

Thompson-Eagle, E.T., Frankenberger Jr., W.T., 1990. Protein-mediated selenium biomethylation in evaporation pond water. Environmental Toxicology and Chemistry 9, 1453−1462.

Thompson-Eagle, E.T., Frankenberger Jr., W.T., 1992. Bioremediation of soils contaminated with selenium. In: Lal, R., Stewart, B.A. (Eds.), Advances in Soil Science. Springer-Verlag, New York, pp. 261−310.

Wilber, E.G., 1980. Toxicology of selenium: a review. Clinical Toxicology 17, 171−230.

Zhang, Y.Q., Frankenberger Jr., W.T., Moore, J.N., 1999. Effect of soil moisture on DMeSe transport and transformation to nonvolatile Se. Environmental Science and Technology 33, 3415−3470.

Zawislanski, P.T., Benson, S.M., Terberg, R., Borglin, S.E., 2003. Selenium speciation, solubility, and mobility in land-disposed dredged sediments. Environmental Science and Technology 37, 2415−2420.

Zayed, A., Pilon-Smith, E., Lin, Z.-Q., Terry, N., 2000. In: Terry, N., Bañuelos, G.S. (Eds.), Phytoremediation of Metal-contaminated Water and Soils. CRC Press, Boca Raton, FL, pp. 63−86.

Zhang, Y.Q., Frankenberger Jr., W.T., 1999. Effects of soil moisture, depth, and organic amendments on selenium volatilization. Journal of Environmental Quality 28, 1321−1326.

Zieve, R., Peterson, P.J., 1981. Factors influencing the volatilization of selenium from soil. Science of the Total Environment 19, 277−284.

Zieve, R., Peterson, P.J., 1984. Volatilization of selenium from plants and soils. Science of the Total Environment 32, 197−202.